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SOME NEW OR LITTLE-USED INSECTICIDES WORTHY OF FURTHER TESTING

Part I. Copper-Arsenic Compounds1/

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The history of several of our most potent and useful insecticides reveals that many years frequently elapse between the first published account of them and their general adoption. For example, derris was mentioned as an insecticide in 1848, and a study of its possibilities was reported in 1919, but it was not used in quantity in the United States until 1931. Tartar emetic was tested as an insecticide in 1890, but did not come into large-scale use until about 1936.

The writer believes that the time between the initial discovery of the insecticidal action of a material and its commercial adoption could be greatly shortened by proper publicity. When sufficient information on the insecticidal value of a material is published, its commercial production will be eagerly undertaken by the chemical industry and it will be made available for public use. The first step in this plan is to stimulate interest among entomologists so that many tests against different insects will be made. In the present series of papers an effort is made to bring to the attention of entomologists materials not now used commercially as insecticides, but which are believed to possess possibilities for insect control that should be further explored.

Compounds Related to Paris Green

Paris green is one of our oldest insecticides and, in spite of competition from the newer arsenicals such as lead arsenate, calcium arsenate, and zinc arsenite, it is still consumed to the extent of about 2 million pounds annually. It has the formula $3CuAs_2O_4.Cu(CH_3COO)_2$ and contains 58.55 percent of arsenic trioxide, 31.39 percent of cupric oxide (equivalent to 25.08 percent of copper), and 10.06 percent of acetic acid anhydride.

1/ Free use has been made of unpublished data obtained by E. H. Siegler, of the Division of Fruit Insect Investigations, and M. C. Swingle and associates, of the Division of Control Investigations. Grateful acknowledgment is made to these Divisions for permission to use their results.

Dearborn (1, 2) has prepared compounds analogous to paris green using such acids of the acetic series as formic, propionic, butyric, mono-, di-, and trichloroacetic, lauric, palmitic, stearic, and melissic. These greens are made by adding a hot aqueous solution of a soluble copper salt, such as copper sulfate, to a hot solution of sodium arsenite mixed with a hot solution of an alkali-metal salt of the fatty acid (i.e., a soap) and heating. Unsaturated acids, such as crotonic, oleic, erucic, linoleic, and linolenic, and also mixed acids resulting from the saponification of vegetable or animal oils can be similarly used (3, 4, 5, 6, 7). Acids from the following oils have also been employed to prepare copper-arsenic compounds: Castor, coconut, cottonseed, corn, linseed, menhaden, palm, peanut, rapeseed, sesame, soybean, and tung.

The insecticidal values of these greens have been tested only to a limited extent. Fleming and Baker (12) tested paris green and a number of its homologues in comparison with lead arsenate for the control of the adult Japanese beetle (*Popillia japonica* Newm.). Potted smartweed plants were sprayed with each arsenical in several concentrations and then placed in glass cages under controlled temperature, relative humidity, and light. Freshly collected Japanese beetles that had been starved for 6 hours were distributed in each cage, and after 48 hours a record was made of beetle mortality and spray injury. Their results for a concentration of 8 pounds per 100 gallons are as follows:

Material	Coefficient of effectiveness	Injury to foliage
Lead arsenate	1.00	Slight
Copper crotonoarsenite	.73	Moderate
Paris green	.68	Slight
Copper palmitoarsenite	.64	Slight
Paris green and flour	.60	Moderate
Tung-oil green	.56	Slight
Cottonseed-oil green	.55	Moderate
Paris green and summer oil	.54	Slight
Copper lauroarsenite	.38	Severe
Soybean-oil green	.28	Slight
Copper stearoarsenite	.24	Very slight
Copper oleoarsenite	.24	Slight
Rapeseed-oil green	.09	Moderate

Fassig and Campbell (11) tested the effectiveness of some of these greens against the confused flour beetle (*Tribolium confusum* Duv.) by placing young beetles in a mixture of 10 parts of insecticide and 90 parts of finely milled whole-wheat flour for 24 hours, with the following results:

Series 1

Material	Percent mortality
Copper stearoarsenite	88
Soybean-oil green	84
Linseed-oil green	83
Fish-oil green	56
Copper oleoarsenite	27
Lead arsenate	7

Series 2

Material	Percent mortality
Copper crotonoarsenite	98
Copper lauroarsenite	92
Peanut-oil green	91
Copper monochloroacetoarsenite	64
Copper dichloroacetoarsenite	62
Paris green	51
Lead arsenate	11

The greater effectiveness of some of these compounds was attributed in part to better adhesiveness and to a possible difference in particle size. Several of these greens were tested in the laboratory by J. B. Gahan and A. M. Phillips, at Sanford, Fla., under the direction of M. C. Swingle, against fourth instars of the southern armyworm (Prodenia eridania (Cram.)) and fifth instars of the fall webworm (Hyphantria cunea (Drury)) and the melonworm (Diaphania hyalinata (L.)). Cooper oleoarsenite and greens prepared from fish oil, tung oil, peanut oil, and linseed oil were effective against the southern armyworm and the melonworm but were ineffective against the fall webworm. No significant and consistent differences between these greens were detected.

Against larvae of the codling moth (Carpocapsa pomonella L.) the following results were obtained by Dr. Siegler in laboratory tests at Beltsville, Md., when he used these greens at the rate of 4 pounds per 100 gallons:

Material	Percentage of apple plugs	
	Wormy	Stung
Fish-oil green	1.9	0.0
Peanut-oil green	1.0	5.9
Copper oleoarsenite	5.7	1.9
Linseed-oil green	9.6	5.8
Tung-oil green	14.0	3.2
Copper phenylstearoarsenite	23.6	17.9

Compounds Made with Sulfurized Organic Acids

When an unsaturated organic acid, such as oleic, is heated with sulfur at about 200° C., with a little iodine added as a catalyst, 1 atom of sulfur is taken up by each double bond of the acid. Clupanodonic acid from fish oil, which contains 4 double bonds, may theoretically combine with 1, 2, 3, or 4 atoms of sulfur under the same treatment. The resulting sulfurized acids may be combined with copper and arsenic in the same way as the unsulfurized fatty acids (8). Free fatty acids, obtained by saponifying a vegetable, animal, or fish oil, may be sulfurized and used in this process. Examples are the acids from peanut, linseed, fish, and tung oils (9, 10). The sulfur in the greens prepared from these sulfurized acids ranges from about 4 to 10 percent, the arsenic trioxide from 36 to 39 percent, and the copper oxide from about 19 to 21 percent. These products are of a dirty green color, have a greasy feel, are insoluble in water, and require the addition of a wetting agent.

Swingle and associates found that copper sulfoleoarsenite, containing 29.8 percent of arsenic trioxide, 5.2 percent of sulfur, and 17.8 percent of copper, when applied as a dust was effective against the Australian cockroach (*Periplaneta australasiae* (F.)), the banded cucumber beetle (*Diabrotica balteata* Lec.), the cross-striped cabbage worm (*Evergestis rimosalis* (Guen.)), and the imported cabbage worm (*Pieris rapae* L.), but was ineffective against the melonworm, larvae of the Mexican bean beetle (*Epilachna varivestis* (Muls.)), and the adult squash bug (*Anasa tristis* (Deg.)), and only partly effective against mosquito (*Culex* spp.) larvae (73 percent mortality in 18 hours at 100 p.p.m.). When this material was tested by Dr. Siegler against codling moth larvae by the apple plug method at a concentration of 4 pounds per 100 gallons, 7.5 percent of the plugs were wormy and none were stung. Lead arsenate usually gives about 40 percent of wormy and stung apple plugs at the same concentration.

Greens made from sulfurized tung oil, fish oil, and linseed oil, when tested against the same insect, gave 13.9, 15.7, and 18.2 percent of wormy fruit and 1.9, 4.9, and 6.1 percent of stung fruit

Effect of Greens on Apple Foliage

Dr. Siegler sparyed greens made from fish, peanut, linseed, and tung oils, and also from sulfurized fish, linseed, and tung oils and copper oleoarsenite and copper phenylstearoarsenite, upon young Stayman and Grimes Golden apple trees at Beltsville, Md. The concentration of these sprays was 4 pounds per 100 gallons of water. The foliage was injured in every instance, and the peanut-oil green defoliated the tree Whether this tendency to cause serious injury could be overcome by the addition of hydrated lime or other "safener" designed to lessen the effects of soluble arsenicals has not yet been determined.

The above greens and also those made from sulfurized corn, soybean, and peanut oils were tested in the laboratory by Swingle and associates

against one or more of the following insects. Banded cucumber beetle, Colorado potato beetle (Leptinotarsa decemlineata (Say)), cross-striped cabbage worm, imported cabbage worm, melonworm, mosquito larvae, southern armyworm, and southern beet webworm (Pachyzancla bipunctalis (F.)). The mortality was practically 100 percent for all species except mosquito larvae, which exhibited mortalities of 76 to 94 percent following applications of 100 p.p.m.

Suggested Uses

The foregoing results clearly show that these compounds are very toxic to insect pests. As their physical properties, such as wettability, adhesiveness, etc., vary with the type of acid employed (saturated, unsaturated, halogenated, etc.), and also with the arsenic and copper content and the solubility, a series of new insecticides possessing a wide range of physical and chemical properties is available.

The following uses for these greens are suggested:

(1) The green made from formic acid contains the most arsenic (60.22 percent As_2O_3) and should be superior to paris green in insuring a quick kill of cotton flea hoppers, bollworms, boll weevils, cotton leaf worms, Colorado potato beetles, and other insect pests of plants that are resistant to soluble arsenicals.

(2) The greens made from oleic or stearic acid or from the fatty acids from peanut, soybean, or other vegetable oils yield but little soluble arsenic when added to water and are worthy of testing as substitutes for lead arsenate for combating certain insects. It will be necessary to add a little wetting agent to these greens because of their greasy character, and also a safener to lessen the effects of soluble arsenic and soluble copper upon the foliage of some plants. If the tendency to injure apple foliage can be overcome, these materials would also be worth testing against the codling moth.

(3) The same greens, because they remain floating on water longer, should prove superior to paris green for the control of surface-feeding mosquitoes.

(4) These oil greens are wetted by petroleum oils. A product made by grinding one of these greens in a petroleum spray oil and emulsifying in water offers possibilities for the control of insects now combated by lead arsenate-oil sprays.

(5) All these greens contain a considerable amount of copper (25.79 percent as a maximum in formic green), which should display the characteristic fungicidal action of this metal.

Summary

Many compounds analogous to paris green have been prepared by substituting other organic acids for acetic acid. Such acids may be substituted by halogen or other radicals, or, if unsaturated, they may have an atom of sulfur added to each double bond. Methods of making these compounds, called "greens," have been described by Dearborn. Tests made by entomologists with several representatives of different classes of these greens have shown the following results:

Insect	Toxicity under laboratory conditions
Australian cockroach	Toxic
Banded cucumber beetle	Toxic
Codling moth (larvae)	Superior to lead arsenate
Colorado potato beetle	Toxic
Confused flour beetle	Superior to lead arsenate
Cross-striped cabbage worm	Toxic
Fall webworm	Nontoxic
Imported cabbage worm	Toxic
Japanese beetle	Inferior to lead arsenate
Melonworm	Toxic
Mexican bean beetle (larvae)	Nontoxic
Mosquitoes (larvae)	Toxic
Southern armyworm	Toxic
Southern beet webworm	Toxic
Squash bug (adults)	Nontoxic

Literature Cited

(1) Dearborn, F. E.
1935. Homologs of paris green. I. Lower members of the acetic acid series. Jour. Econ. Ent. 28: 710-714.

(2) -------
1936. Homologs of paris green. II. Higher members of the acetic acid series. Jour. Econ. Ent. 29: 445-449.

(3) -------
1937. Homologs of paris green. III. Members of the oleic and linoleic acid series. Jour. Econ. Ent. 30:140-143.

(4) -------
1937. Homologs of paris green. IV. Insecticides prepared from animal and vegetable oils. Jour. Econ. Ent. 30:958-962.

(5) -------
1937. Double salt of copper arsenite and copper salt of an unsaturated fatty acid and process of making the same. U. S. Patent 2,080,004; issued May 11.

(6) Dearborn, F. E.
1938. Double salts of copper arsenite and a copper salt of a higher unsaturated fatty acid. U. S. Patent 2,104,584; issued January 4.

(7) -------
1938. Insecticide and fungicide. U. S. Patent 2,127,380; issued August 16.

(8) -------
1939. Compounds of copper, arsenic, and a sulfmonocarboxylic acid and process of making them. U. S. Patent 2,159,585; issued May 23.

(9) -------
1939. Processes of treating glycerides. U. S. Patent 2,169,793; issued August 15.

(10) -------
1940. Insecticide and fungicide. U. S. Patent 2,201,103; issued May 14.

(11) Fassig, W. W., and Campbell, F. L.
1937. Relative effectiveness of homologs of paris green against confused flour beetle. (Scientific Note) Jour. Econ. Ent. 30:681-682.

(12) Fleming, W. E., and Baker, F. E.
1936. Paris green and its homologues as insecticides against the Japanese beetle. Jour. Agr. Res. 53:187-195.